TECHNICAL MEMORANDUM



TO: Jim Homolya / OAQPS

FROM: Michael S. Clark / NAREL

COPY: Dr. John Griggs / NAREL

DATE: November 19, 2002

SUBJECT: Performance Evaluation of R&P 8400 Ambient Air Monitors

Executive Summary

Five sites located in different states are currently operating at least one of the 8400 series ambient air monitors manufactured by R&P. The 8400N and the 8400S units are designed to capture PM_{2.5} from the ambient air and provide measurement of nitrate and sulfate respectively, every tenminutes. Aqueous spike solutions were recently used to evaluate performance of these semi-continuous monitors. Five blind spikes were analyzed in triplicate by each instrument. All five sites were given the same set of PE samples which covered slightly more than the normal range of instrument calibration. The operators were instructed to analyze the local blank water and the local calibration standard along with the PE samples. Scatter plots were prepared for each monitor showing the mass of analyte reported versus the mass of analyte spiked into the instrument. Similar results for the PE solutions were observed from all of the sites even though each instrument produced a slightly different efficiency for generating and analyzing the signal pulse from the aqueous spike.

To further examine the data reported from the sites, a linear calibration curve based upon analysis of the PE solutions was generated for each instrument, and new results were calculated. Based upon the new results from the calibration curves, all sites can achieve good accuracy for aqueous spikes over the concentration range tested.

This study has revealed a possible discrepancy between the local nitrate solutions and the PE solutions. The local nitrate solution at all five sites has a nominal concentration of 100 ng/\mu L , but its grand average value determined by measurement at all sites was $121 \pm 20 \text{ ng/\mu L}$ (uncertainty = 2 x pooled standard deviation). One of the PE solutions also had a nominal concentration of 100 ng/\mu L for nitrate, and its grand average determined by all sites was $104 \pm 14 \text{ ng/\mu L}$. Further analysis of these two solutions was performed using the Wilcox matched-pairs signed-rank test. The null hypothesis which states that both solutions are identical must be rejected at the 95% confidence interval, but may not be rejected at the 99% confidence interval. Some followup may be needed to resolve this issue. The local nitrate solution utilized at each site could be re-validated using ion chromatography.

More PE samples are planned at quarterly intervals over the next year.

Experimental Design

Blind aqueous spike solutions were prepared at the National Air and Radiation Environmental Laboratory (NAREL) located in Montgomery, AL. All PE solutions were prepared from the same salts and chemicals that are present in the local calibration solutions used at each field site. Nitrate PE solutions were prepared using KNO₃ and 18 mega-ohm laboratory water which was passed through a 0.2-µm membrane filter immediately before use. Sulfate PE solutions were prepared by dissolving NH₄SO₄ and oxalic acid into the same laboratory water previously described. The oxalic acid was added to each sulfate solution at a rate of 4 mg of carbon (from the oxalic acid) per 3 mg of sulfate (from the NH₄SO₄). All PE solutions were analyzed using a Dionex DX500 Ion Chromatograph configured for the analysis of anions. All PE solutions were verified to be within 5 % of the nominal concentration of nitrate and sulfate before they were shipped to the site operator. The concentration of nitrate and sulfate present in each PE solution is listed in Table 2 and Table 4 respectively, at the end of this report.

A new syringe was provided to each site operator with instructions to use the new syringe for all spiking during this study. Normally each instrument is calibrated by injecting different volumes of one [local] spike solution to establish the calibration range. For this study five PE solutions were provided for each instrument to establish a calibration range using only one spike volume. The purpose for using only one spike volume was to keep the amount of water deposited onto the flash strip constant for all spikes.

The site operator was instructed to perform a manual audit of the pulse analyzer before starting the aqueous spikes. Audit results from the 8400N and the 8400S are presented in Table 1 and Table 3 respectively, at the end of this report.

Analysis of Aqueous Nitrate Spike Solutions

Site operators were instructed to perform triplicate analysis of the aqueous solutions using only one spike volume, 0.5 μ L. The analysis began with the local blank water followed by analysis of the local 100 ng/ μ L nitrate standard. The study continued by running the five *blind* solutions identified simply as N1 through N5. The results reported from the sites are included in Table 2 at the end of this report along with the previously undisclosed concentration of N1 through N5. An extra column of "Re-calculated Results" has also been added to Table 2. Results from each site were recalculated from a calibration curve based upon the PE solutions analyzed at that site. By recalculating all results from a calibration curve, the new results are corrected for inefficient pulse generation and analysis.

Results from a single site are presented as a scatter plot in Figure 1 through Figure 5. The mass measured versus the mass deposited is plotted for each spike. Results from the PE solutions are colored red in the plots, and results from the local blank water and local $100 \text{ ng/}\mu\text{L}$ solution are presented in blue. Each plot also shows a green "One-to-One" line which represents perfect agreement between the mass measured and the mass deposited.

Figure 1

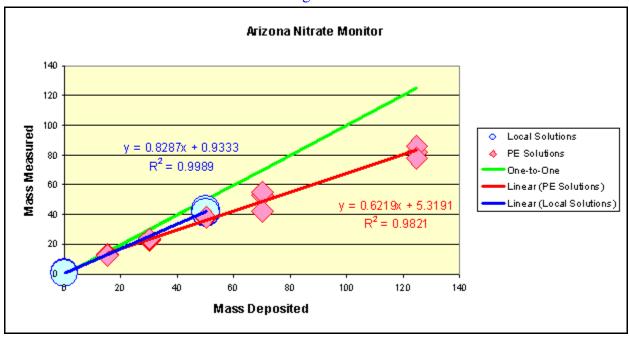


Figure 2

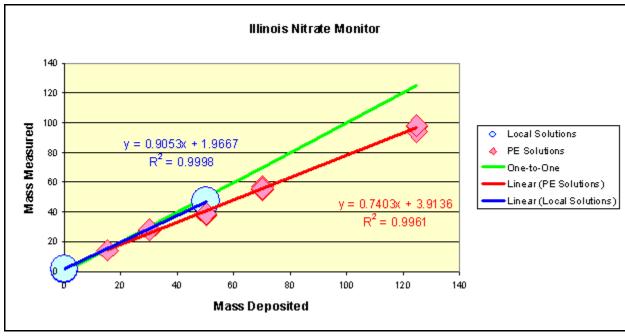


Figure 3

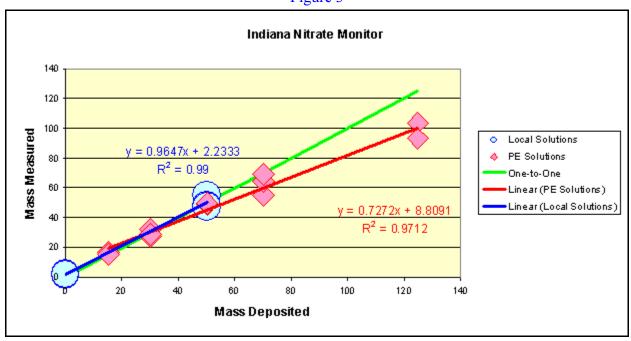


Figure 4

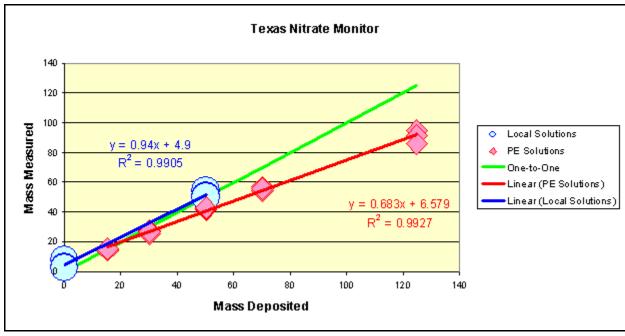


Figure 5

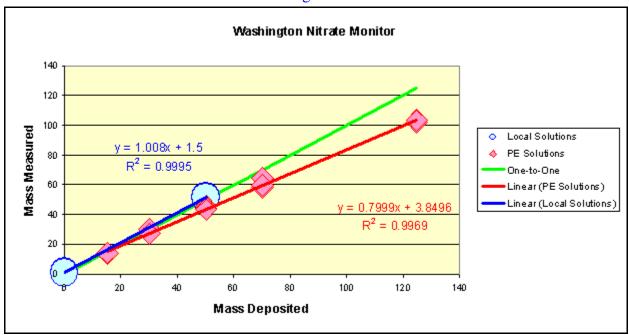
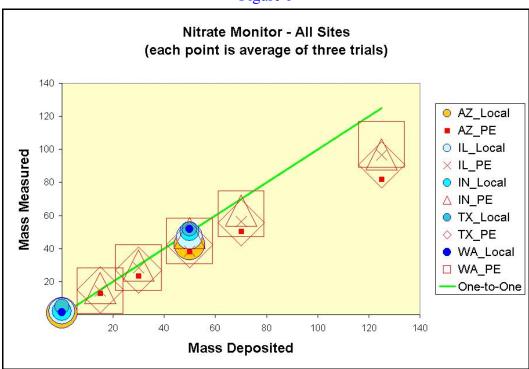


Figure 6 contains results from all five sites. To simplify the graph, each point represents an average result from three replicate spikes of the same spike solution. Each site is represented by a different symbol as shown in the plot legend.

Figure 6



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Figure 7

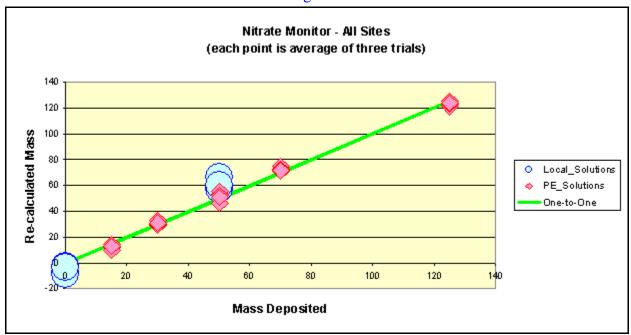


Figure 7 shows re-calculated mass from all of the sites. Results were re-calculated from a calibration curve established at each instrument by the analysis of PE samples. This graph clearly shows an apparent difference between the 100 ng/ μ L PE solution and the Local 100 ng/ μ L solution. Also notice how well the PE solutions fit the green One-to-One line.

Analysis of Aqueous Sulfate Spike Solutions

The Arizona site did not operate a sulfate monitor for this study. Therefore only four sites reported sulfate results. Site operators were instructed to perform triplicate analysis of the aqueous solutions using only one spike volume, $0.2~\mu L$. The analysis began with the local blank water followed by analysis of the local 300 ng/ μL sulfate standard. The study continued by running the five *blind* solutions identified simply as S1 through S5. The results reported from the sites are included in Table 4 at the end of this report along with the previously undisclosed concentration of S1 through S5. An extra column of "Re-calculated Results" has also been added to Table 4. Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site. By re-calculating all results from a calibration curve, the new results are corrected for inefficient pulse generation and analysis.

Results from a single site are presented as a scatter plot in Figure 8 through Figure 13. The mass measured versus the mass deposited is plotted for each spike. Results from the PE solutions are colored red in the plots, and results from the local blank water and local 300 ng/ μ L solution are presented in blue. Each plot also shows a green "One-to-One" line which represents perfect agreement between the mass measured and the mass deposited.

Figure 8

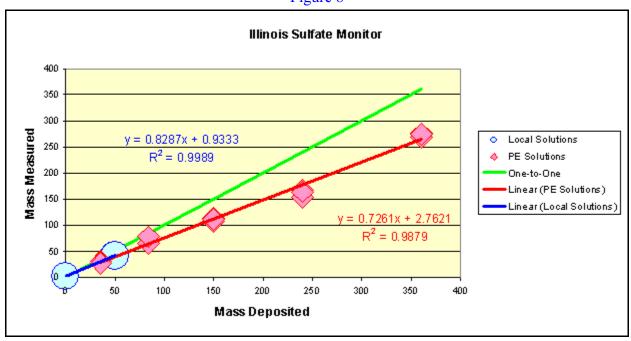


Figure 9

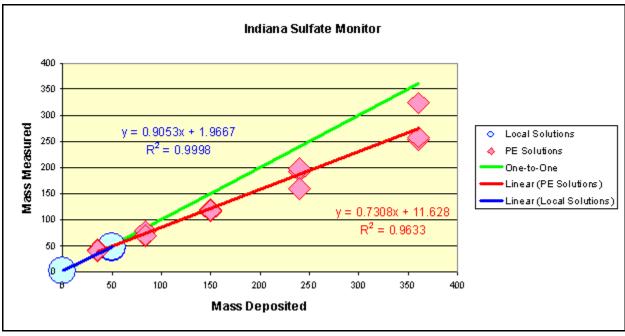


Figure 10

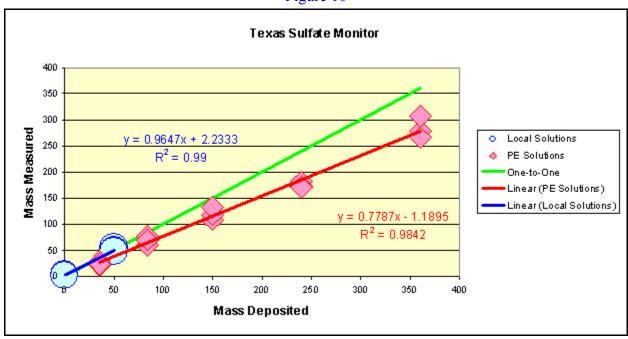


Figure 11

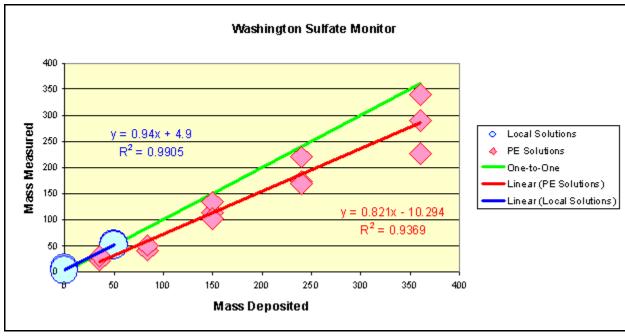


Figure 12

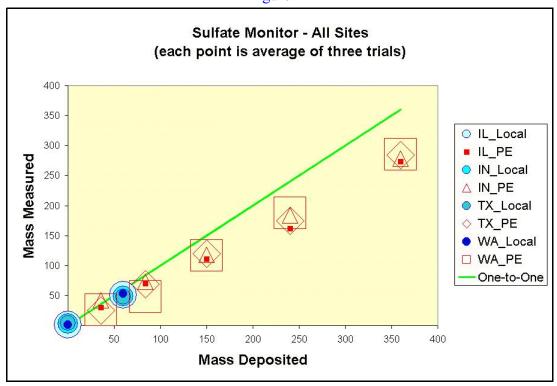


Figure 12 contains results from all four sites. To simplify the graph, each point represents an average result from three replicate spikes of the same spike solution. Each site is represented by a different symbol as shown in the plot legend.

Figure 13

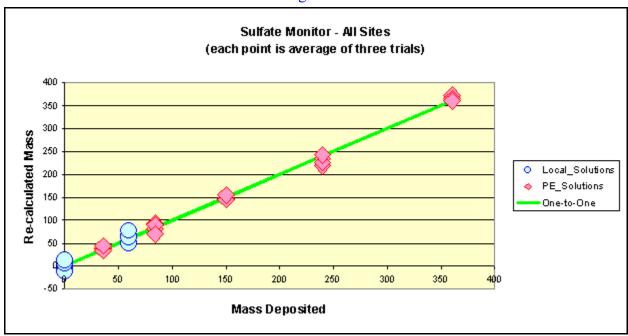


Figure 13 shows re-calculated mass from all of the sites. Results were re-calculated from a calibration curve established at each instrument by the analysis of PE samples. Again, notice how well the re-calculated results in Figure 13 fit the green One-to-One line, but the uncorrected results in Figure 12 consistently fall below the One-to-One line.

Conclusions

Analysis of these blind aqueous PE solutions have demonstrated reasonably good analytical precision from all of the participating sites. Results generated by the aqueous spikes are used to correct ambient air cycle data for inefficient pulse generation and analysis.

This study has revealed a possible discrepancy between the local nitrate solutions and the PE solutions. Considering the importance of the local aqueous spike solution in the overall analytical scheme, the field solutions should be evaluated for accuracy at NAREL using ion chromatography.

All stakeholders are encouraged to offer suggestions for improving our next PE study.

Table 1. Evaluation of the 8400N Pulse Analyzer

Site	Audit Date	Audit Time	*** Span Gas Conc. (ppb)	Steady State Check (ppb)	Flow Balance Check (ppb)	Line Purge (ppb)	NOx Pulse Read (ppb*s)	Age of Flash Strip (days)	
Arizona	08-Oct-02	4:05 PM	4910	4539.1	3944.2	0	2630.7	4	
Illinois	24-Oct-02	7:30 AM	5240	5468.1	4759.9	2.1	3587.9	17	
Indiana	10-Oct-02	9:20 AM	5100	5022	4501.7	1	2971.4	9	
Texas	10-Oct-02	1:20 PM	5593	5363	4780.1	0.7	2990.7	5	
Washington	15-Oct-02	7:40 AM	5120	5126.9	4570.1	2.4	3025.6	12	
	*** Span gas concentration as labeled on the bottle (should be 5000 ppb).								

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Arizona	Local blank water	0.5	0	-4.9	30.4	1.1	0.84	-6.8
Arizona	Local blank water	0.5	0	-7.8	24.4	0.9	0.84	-7.1
Arizona	Local blank water	0.5	0	-9.8	21.6	0.8	0.84	-7.3
Arizona	Local 100 ng/µL std	0.5	50	-12.8	1170.5	41.5	0.84	58.2

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Arizona	Local 100 ng/µL std	0.5	50	-4.1	1232.5	43.7	0.84	61.7
Arizona	Local 100 ng/µL std	0.5	50	4.6	1180.8	41.9	0.84	58.8
Arizona	N1	0.5	15	-8.4	372.6	13.2	0.84	12.7
Arizona	N1	0.5	15	-13.4	373.3	13.2	0.84	12.7
Arizona	N1	0.5	15	-3.6	362.9	12.9	0.84	12.2
Arizona	N2	0.5	30	-10.9	636.7	22.6	0.84	27.8
Arizona	N2	0.5	30	-12.6	667.5	23.7	0.84	29.6
Arizona	N2	0.5	30	-21.8	681.9	24.2	0.84	30.4
Arizona	N3	0.5	50	10	1072.2	38	0.84	52.6
Arizona	N3	0.5	50	-6.3	1078	38.3	0.84	53.0
Arizona	N3	0.5	50	-2.6	1086.2	38.5	0.84	53.4
Arizona	N4	0.5	70	-7.8	1497.9	53.2	0.84	77.0
Arizona	N4	0.5	70	-6	1552	55.1	0.84	80.1
Arizona	N4	0.5	70	-21.1	1196.2	42.4	0.84	59.6
Arizona	N5	0.5	125	-2.4	2304.7	81.8	0.84	123.0
Arizona	N5	0.5	125	3.8	2419.4	85.8	0.84	129.4

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Arizona	N5	0.5	125	-10.7	2196	77.9	0.84	116.7
Illinois	Local blank water	0.5	0	46.4	40.4	1.5	0.85	-3.3
Illinois	Local blank water	0.5	0	36.6	62.3	2.2	0.85	-2.3
Illinois	Local blank water	0.5	0	28.5	61.3	2.2	0.85	-2.3
Illinois	Local 100 ng/μL std	0.5	50	23	1319.8	47.5	0.85	58.9
Illinois	Local 100 ng/μL std	0.5	50	30.6	1304.8	46.9	0.85	58.1
Illinois	Local 100 ng/μL std	0.5	50	25.8	1315	47.3	0.85	58.6
Illinois	N1	0.5	15	25.6	398.4	14.3	0.85	14.0
Illinois	N1	0.5	15	27.8	402.5	14.5	0.85	14.3
Illinois	N1	0.5	15	22.9	403.3	14.5	0.85	14.3
Illinois	N2	0.5	30	28.3	796.9	28.7	0.85	33.5
Illinois	N2	0.5	30	30.1	780.6	28.1	0.85	32.7
Illinois	N2	0.5	30	24.4	793.2	28.5	0.85	33.2
Illinois	N3	0.5	50	25.1	1049.9	37.7	0.85	45.6
Illinois	N3	0.5	50	28.8	1074.5	38.6	0.85	46.9
Illinois	N3	0.5	50	27.9	1089.1	39.2	0.85	47.7

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Illinois	N4	0.5	70	22.7	1602.8	57.6	0.85	72.5
Illinois	N4	0.5	70	30.6	1538.2	55.3	0.85	69.4
Illinois	N4	0.5	70	26.8	1550.7	55.8	0.85	70.1
Illinois	N5	0.5	125	28.2	2713	97.5	0.85	126.4
Illinois	N5	0.5	125	28.2	2625.3	94.4	0.85	122.2
Illinois	N5	0.5	125	23.9	2729.4	98.1	0.85	127.2
Indiana	Local blank water	0.5	0	17.2	72.6	2.7	0.89	-8.4
Indiana	Local blank water	0.5	0	26.7	46.5	1.7	0.89	-9.8
Indiana	Local blank water	0.5	0	26	60.4	2.3	0.89	-9.0
Indiana	Local 100 ng/µL std	0.5	50	20	1475.4	55.2	0.89	63.8
Indiana	Local 100 ng/μL std	0.5	50	18	1304.8	48.8	0.89	55.0
Indiana	Local 100 ng/μL std	0.5	50	21.8	1247.1	47.4	0.89	53.1
Indiana	N1	0.5	15	19.4	454.8	17	0.89	11.3
Indiana	N1	0.5	15	15.9	414.5	15.5	0.89	9.2
Indiana	N1	0.5	15	30.9	410.2	15.4	0.89	9.1
Indiana	N2	0.5	30	36.7	735.3	27.5	0.89	25.7

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Indiana	N2	0.5	30	32.4	868.2	32.5	0.89	32.6
Indiana	N2	0.5	30	31	776.9	29.1	0.89	27.9
Indiana	N3	0.5	50	29.4	1312.4	49.1	0.89	55.4
Indiana	N3	0.5	50	33.4	1308.5	49	0.89	55.3
Indiana	N3	0.5	50	32.5	1333.8	49.9	0.89	56.5
Indiana	N4	0.5	70	27.6	1479.6	55.4	0.89	64.1
Indiana	N4	0.5	70	24.1	1734.9	64.9	0.89	77.1
Indiana	N4	0.5	70	35.6	1845.7	69.1	0.89	82.9
Indiana	N5	0.5	125	27.2	2774.5	103.8	0.89	130.6
Indiana	N5	0.5	125	31.4	2491.2	93.2	0.89	116.0
Indiana	N5	0.5	125	29.9	2496.7	93.4	0.89	116.3
Texas	Local blank water	0.5	0	-1.4	222.6	8.6	0.91	3.0
Texas	Local blank water	0.5	0	-3.8	82.4	3.2	0.91	-4.9
Texas	Local blank water	0.5	0	-47.8	75.8	2.9	0.91	-5.4
Texas	Local 100 ng/µL std	0.5	50	-9	1417.2	54.6	0.91	70.3
Texas	Local 100 ng/µL std	0.5	50	-30.6	1317.6	50.8	0.91	64.7

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Texas	Local 100 ng/µL std	0.5	50	-57.8	1306	50.3	0.91	64.0
Texas	N1	0.5	15	-11.6	396	15.3	0.91	12.8
Texas	N1	0.5	15	-48.6	378.2	14.6	0.91	11.7
Texas	N1	0.5	15	-40.3	407.4	15.7	0.91	13.4
Texas	N2	0.5	30	-10.2	673.6	25.9	0.91	28.3
Texas	N2	0.5	30	-33.8	718.9	27.7	0.91	30.9
Texas	N2	0.5	30	-51	696.8	26.8	0.91	29.6
Texas	N3	0.5	50	-23.4	1092.4	42.1	0.91	52.0
Texas	N3	0.5	50	-11.4	1100.9	42.4	0.91	52.4
Texas	N3	0.5	50	-45.2	1114.3	42.9	0.91	53.2
Texas	N4	0.5	70	-27	1421.1	54.7	0.91	70.5
Texas	N4	0.5	70	-10.4	1478.2	56.9	0.91	73.7
Texas	N4	0.5	70	-44.1	1442.5	55.6	0.91	71.8
Texas	N5	0.5	125	-30.8	2465.3	95	0.91	129.5
Texas	N5	0.5	125	-17.7	2376.7	91.5	0.91	124.3
Texas	N5	0.5	125	-33.2	2227.7	85.8	0.91	116.0

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Washington	Local blank water	0.5	0	46.3	62.7	2.4	0.91	-1.8
Washington	Local blank water	0.5	0	36.2	26.6	1	0.91	-3.6
Washington	Local blank water	0.5	0	29.2	27.5	1.1	0.91	-3.4
Washington	Local 100 ng/μL std	0.5	50	28.9	1364.2	52.5	0.91	60.8
Washington	Local 100 ng/μL std	0.5	50	24.1	1331.8	51.2	0.91	59.2
Washington	Local 100 ng/µL std	0.5	50	37.3	1351.9	52	0.91	60.2
Washington	N1	0.5	15	30.4	379.2	14.6	0.91	13.4
Washington	N1	0.5	15	31.2	365.8	14.1	0.91	12.8
Washington	N1	0.5	15	26.2	371.6	14.3	0.91	13.1
Washington	N2	0.5	30	33.4	715	27.5	0.91	29.6
Washington	N2	0.5	30	19.8	785.7	30.2	0.91	32.9
Washington	N2	0.5	30	34.8	710.9	27.4	0.91	29.4
Washington	N3	0.5	50	24	1184.9	45.6	0.91	52.2
Washington	N3	0.5	50	25.5	1153	44.4	0.91	50.7
Washington	N3	0.5	50	27.9	1135.4	43.7	0.91	49.8
Washington	N4	0.5	70	28.9	1679.8	64.6	0.91	75.9

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Washington	N4	0.5	70	39.8	1528.2	58.8	0.91	68.7
Washington	N4	0.5	70	29.5	1549.6	59.6	0.91	69.7
Washington	N5	0.5	125	25.8	2657	102.2	0.91	122.9
Washington	N5	0.5	125	31.7	2688.5	103.5	0.91	124.6
Washington	N5	0.5	125	23.5	2682.6	103.2	0.91	124.2

^{***} Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site.

Table 3. Evaluation of the 8400S Pulse Analyzer

Site	Audit Date	Audit Time	*** Span Gas Conc. (ppb)	Steady State Check (ppb)	Flow Balance Check (ppb)	Line Purge (ppb)	Age of Flash Strip (days)			
Arizona										
Illinois	24-Oct-02	9:40 AM	1200	1196.7	1031.3	-1.1	8			
Indiana	15-Oct-02	9:35 AM	1200	1362.3	1157.8	3.9	6			
Texas	10-Oct-02	1:20 PM	912	944.2	823.7	1.4	5			
Washington	09-Oct-02	8:10 AM	1089	1078.5	928	0.2	1			
	*** Span gas concentration as labeled on the bottle (should be 1000 ppb).									

Table 4. Aqueous Sulfate Standards

Site	Sample ID	Volume Deposited (uL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Illinois	Local blank water	0.2	0	-66	13	1	1.13	-2.4
Illinois	Local blank water	0.2	0	-94.8	17.2	1.3	1.13	-2.0
Illinois	Local blank water	0.2	0	-85.6	11.3	0.8	1.13	-2.7
Illinois	Local 300 ng/µL std	0.2	60	-69.9	713.5	52.9	1.13	69.1

Table 4. Aqueous Sulfate Standards

Site	Sample ID	Volume Deposited (uL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Illinois	Local 300 ng/µL std	0.2	60	-89.3	611	45.3	1.13	58.6
Illinois	Local 300 ng/µL std	0.2	60	-90.4	736.8	54.6	1.13	71.4
Illinois	S1	0.2	36	-77.4	436.9	32.4	1.13	40.8
Illinois	S1	0.2	36	-73.1	401.7	29.8	1.13	37.2
Illinois	S1	0.2	36	-87.4	372.6	27.6	1.13	34.2
Illinois	S2	0.2	84	-78.2	890.8	66	1.13	87.1
Illinois	S2	0.2	84	-77.9	890.4	66	1.13	87.1
Illinois	S2	0.2	84	-87.3	1049	77.7	1.13	103.2
Illinois	S3	0.2	150	-85.8	1431.7	106.1	1.13	142.3
Illinois	S3	0.2	150	-85.9	1529.5	113.3	1.13	152.2
Illinois	S3	0.2	150	-74.7	1514.9	112.3	1.13	150.9
Illinois	S4	0.2	240	-72.7	2072.5	153.6	1.13	207.7
Illinois	S4	0.2	240	-72.1	2261.2	167.6	1.13	227.0
Illinois	S4	0.2	240	-72	2224.7	164.9	1.13	223.3
Illinois	S5	0.2	360	-65.2	3642.5	269.9	1.13	367.9
Illinois	S5	0.2	360	-85.2	3716.8	275.4	1.13	375.5

Table 4. Aqueous Sulfate Standards

Site	Sample ID	Volume Deposited (uL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Illinois	S5	0.2	360	-73.4	3696.1	273.9	1.13	373.4
Indiana	Local blank water	0.2	0	77.4	75.9	4.6	0.94	-9.6
Indiana	Local blank water	0.2	0	96.9	32	2	0.94	-13.2
Indiana	Local blank water	0.2	0	83.4	50.6	3.1	0.94	-11.7
Indiana	Local 300 ng/µL std	0.2	60	-70.2	924.2	56.6	0.94	61.5
Indiana	Local 300 ng/µL std	0.2	60	32.6	728.2	44.6	0.94	45.1
Indiana	Local 300 ng/µL std	0.2	60	1.7	614.2	44.6	0.94	45.1
Indiana	S1	0.2	36	130.8	663.2	40.6	0.94	39.6
Indiana	S1	0.2	36	56.9	704.5	43.2	0.94	43.2
Indiana	S1	0.2	36	94.2	685.5	42	0.94	41.6
Indiana	S2	0.2	84	140.3	1272	77.9	0.94	90.7
Indiana	S2	0.2	84	97.4	1124	68.9	0.94	78.4
Indiana	S2	0.2	84	105.4	1148	70.3	0.94	80.3
Indiana	S3	0.2	150	112.4	1948.7	119.4	0.94	147.5
Indiana	S3	0.2	150	94.2	1901.9	116.5	0.94	143.5
Indiana	S3	0.2	150	28.4	1927.7	118.1	0.94	145.7

Table 4. Aqueous Sulfate Standards

Site	Sample ID	Volume Deposited (uL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Indiana	S4	0.2	240	31.6	3152.4	193.1	0.94	248.3
Indiana	S4	0.2	240	58.6	3225.2	197.6	0.94	254.5
Indiana	S4	0.2	240	96.8	2604.9	159.6	0.94	202.5
Indiana	S5	0.2	360	10.1	5271.1	322.9	0.94	425.9
Indiana	S5	0.2	360	59.7	4145.4	253.9	0.94	331.5
Indiana	S5	0.2	360	13.5	4209.7	257.9	0.94	337.0
Texas	Local blank water	0.2	0	10.2	144.2	13.2	1.4	18.5
Texas	Local blank water	0.2	0	33.8	9	0.8	1.4	2.6
Texas	Local blank water	0.2	0	45.9	18.6	-1.7	1.4	-0.7
Texas	Local 300 ng/µL std	0.2	60	16.4	458.6	41.9	1.4	55.3
Texas	Local 300 ng/µL std	0.2	60	18.2	458.7	41.9	1.4	55.3
Texas	Local 300 ng/µL std	0.2	60	1.2	658.7	60.3	1.4	79.0
Texas	S1	0.2	36	6.2	305.1	27.9	1.4	37.4
Texas	S1	0.2	36	21.7	235.1	21.5	1.4	29.1
Texas	S1	0.2	36	21.6	269.3	24.6	1.4	33.1
Texas	S2	0.2	84	9.4	840.6	76.9	1.4	100.3

Table 4. Aqueous Sulfate Standards

Site	Sample ID	Volume Deposited (uL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Texas	S2	0.2	84	12.4	642.3	58.7	1.4	76.9
Texas	S2	0.2	84	17.7	769	70.3	1.4	91.8
Texas	S3	0.2	150	13.9	1181.8	108.1	1.4	140.3
Texas	S3	0.2	150	32	1292.7	118.2	1.4	153.3
Texas	S3	0.2	150	18.8	1439.8	131.7	1.4	170.7
Texas	S4	0.2	240	18.2	1991.1	182.1	1.4	235.4
Texas	S4	0.2	240	3.9	1883.3	172.2	1.4	222.7
Texas	S4	0.2	240	6.4	1864.2	170.5	1.4	220.5
Texas	S5	0.2	360	19	3043	278.3	1.4	358.9
Texas	S5	0.2	360	15	3357.7	307	1.4	395.8
Texas	S5	0.2	360	9.3	2915.7	266.6	1.4	343.9
Washington	Local blank water	0.2	0	-3.3	6.2	0.5	1.35	13.1
Washington	Local blank water	0.2	0	-14.2	14	1.2	1.35	14.0
Washington	Local blank water	0.2	0	-19.2	12.9	1.1	1.35	13.9
Washington	Local 300 ng/µL std	0.2	60	-15.9	666.6	58.8	1.35	84.2
Washington	Local 300 ng/µL std	0.2	60	-12.2	519.2	45.8	1.35	68.3

Table 4. Aqueous Sulfate Standards

Site	Sample ID	Volume Deposited (uL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Washington	Local 300 ng/µL std	0.2	60	-4.4	625.4	55.2	1.35	79.8
Washington	S1	0.2	36	-15.3	291	25.7	1.35	43.8
Washington	S1	0.2	36	-4.8	260.2	22.9	1.35	40.4
Washington	S1	0.2	36	-31.7	340.2	30	1.35	49.1
Washington	S2	0.2	84	-20	561.9	49.6	1.35	72.9
Washington	S2	0.2	84	-3	467.3	41.2	1.35	62.7
Washington	S2	0.2	84	-27.5	586.6	51.7	1.35	75.5
Washington	S3	0.2	150	-11.7	1288.1	113.6	1.35	150.9
Washington	S3	0.2	150	-22.4	1516	133.7	1.35	175.4
Washington	S3	0.2	150	-24.5	1151.3	101.5	1.35	136.2
Washington	S4	0.2	240	-27	2495.4	220.1	1.35	280.6
Washington	S4	0.2	240	-30.1	1974.1	174.1	1.35	224.6
Washington	S4	0.2	240	-22	1917.1	169.1	1.35	218.5
Washington	S5	0.2	360	-44.6	3845.2	339.1	1.35	425.6
Washington	S5	0.2	360	-27.3	2572.2	226.9	1.35	288.9
Washington	S5	0.2	360	-24	3280.7	289.3	1.35	364.9

Table 4. Aqueous Sulfate Standards									
Site	Sample ID	Volume Deposited (uL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)	

^{***} Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site.